

PATENT SPECIFICATION

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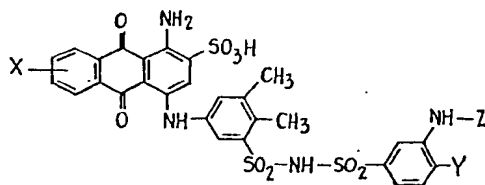


(54) ANTHRAQUINONE DYESTUFFS

(71) We, CIBA-GEIGY A.G., a Swiss Company of CH-4002, Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fibre-reactive anthraquinone dyestuffs, processes for the production of these dyestuffs, their application for the dyeing and printing of textile material, especially that made from natural or regenerated cellulose or polyamide and the textile material when dyed and printed using the dyestuffs.

The fibre-reactive anthraquinone dyestuffs correspond to the general Formula I



(I)

wherein

X and Y represents independently of each other hydrogen or the sulphonic acid group, and

Z represents a fibre reactive radical capable of forming with the substrate at least one covalent bond.

The radical Z can be bound to the substituent —NH— of the dyestuff either directly or by way of bridge members such as, e.g. carbonyl, sulphonyl or carbonyl-imino, whereby the imino hydrogen can be substituted by a lower alkyl group. By "lower" is meant herein containing from 1 to 6 carbon atoms.

Examples of such reactive groups are: the acyl radical of an acid having at least one reactive halogen atom and/or a multiple carbon-carbon bond capable of addition, e.g. the acyl radicals of chloro or bromoacetic acid, β -chloro and β -bromopropionic acid, α,β -dibromopropionic acid, tetrahalogen cyclobutanecarboxylic acid such as 2-chloro-2-fluoro-3,3-difluoro or 2,2,3,3-tetrafluorocyclobutane-1-carboxylic acid, propionic acid, chloropropionic acid, acrylic acid, methacrylic acid, α -chloro, β -chloro, α -bromo and β -bromoacrylic acid, α,β - and β,β -dichloro or α,β - and β,β -dibromoacrylic acid, 2-(2,2,3,3-tetrafluorocyclobutyl-1)-acrylic acid, crotonic acid, α - or β -chloro or α - or β -bromocrotonic acid, α,β -dichlorocrotonic acid, maleic acid, monochloro or monobromomaleic acid, dichloro and dibromomaleic acid, fumaric acid monochloro and monobromofumaric acid, dichloro and dibromofumaric acid, fumaric acid monoester, dichloro and dibromosuccinic acid, vinylsulphonic acid, β -chlorovinylsulphonic acid or a nitrohalogen benzoic acid or nitrohalogen benzene-sulphonic acid having a reactive halogen atom, particularly with fluorine or chlorine in o- or p-position to the nitro group, such as the acyl radical of 3-nitro-4-fluorobenzoic acid or 3-nitro-4-fluorobenzenesulphonic acid; also with strong acids such as hydrochloric acid, sulphuric acid or alkylsulphuric acid, esterified β -hydroxyalkylsulphonyl or β -hydroxyalkylcarbonyl groups such as the β -halogen ethylsulphonyl, β -sulphatoethylsulphonyl or the β -sulphatopropionyl group, the β -alkyl or β -phenyl-

5 sulphonylalkyl-sulphonyl or -carbonyl group, e.g. the β -phenylsulphonylpropionyl group. Preferably, the reactive group is the radical of an aromatic nitrogen hetero-
cycle having advantageously more than one hetero atom in the ring which has at
least one reactive halogen atom such as fluorine, chlorine or bromine, or an acryloyl,
N-hydroxymethylencamino, sulphonic acid or alkylsulphonyl group on a ring carbon
atom.

10 Examples of such reactive groups are: the triazinyl or diazinyl radical having
at least one reactive halogen atom, e.g. the radical of cyanuric chloride, cyanuric
bromide or their primary condensation products, wherein a halogen atom is replaced
by the optionally further substituted radical of a primary or secondary aliphatic,
alicyclic, aromatic or heterocyclic amine, especially by aniline or its sulphonic acid
or carboxylic acid derivatives, by lower mono and dialkylamines, as well as by
15 ammonia, or by the radical of an aliphatic, alicyclic, aromatic or heterocyclic hydroxy
or thiol compound; or the di- or trihalogen pyrimidyl radical such as the 2,4-dichloro,
2,4-dibromo, 2,4-difluoro or, in particular 2,4,5-trichloro, 2,4,5-tribromo or 2,4,5-
trifluoropyrimidyl radical, the 5-bromo or 5-chloro-2,4-difluoro or 5-bromo-2,4-di-
chloropyrimidyl-6-radical and the 2-alkylsulphonylpyrimidyl radical, such as the 2-
methylsulphonyl-4-methylpyrimidyl-6-radical. The dihalogen pyrimidyl radical can
20 carry in the 5-position, e.g. the following substituents: methyl, ethyl, sulphonic acid
amide or carboxylic acid amide optionally substituted at the nitrogen atom, carboxylic
acid methyl or ethyl ester, acyl, e.g. benzoyl, alkenyl, e.g. allyl, chlorovinyl, substituted
alkyl, e.g. carboxymethyl, chloro or bromomethyl, the cyano or nitro group, as well
as the sulphonic acid group.

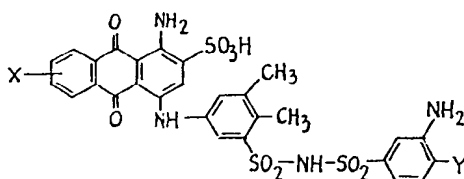
25 Further suitable reactive groups are, e.g. the radical of a dihalogen pyrimidine-
carboxylic acid, of a 2-alkylsulphonyl-4-halogen pyrimidinecarboxylic acid, the radical
of an N-(mono-halogen-bis-alkylamino-s-triazinyl)-carbamic acid such as the N-methyl-
N-(2-chloro-4-dimethylamino-s-triazinyl-6-), the N-ethyl-N-(2-chloro-4-ethylamino-s-
triazinyl-6-), the N-ethyl-N-(2-bromo-4-dimethylamino-s-triazinyl) or the N-ethyl-N-
(2-fluoro-4-diethylamino-s-triazinyl)-carbamic acid or the N-(2-halogeno-4-alkoxy-6-
30 alkylamino-s-triazine)-carbamic acid, the 2,3-dihalogen quinoxalinecarboxylic acid or
-sulphonic acid, the 2-halogen or 2-methylsulphonyl benzothiazole or -oxazole
carboxylic acid or -sulphonic acid, the 1,4-dihalogen phthalazine carboxylic acid, the 2,4-
dihalogen quinazoline carboxylic acid or the 4,5-dihalogen-6-pyridazon-1-yl-alkylene
or -phenylene carboxylic acid, such as the acid radicals of the 2-methylsulphonyl-4-
35 chloropyrimidine-5- or -6-carboxylic acid, 2-ethylsulphonyl-4-chloropyrimidine-5- or
-6-carboxylic acid, 2,4-difluoro or 2,4-dichloropyrimidine-5- or -6-carboxylic acid,
2,4-dichloro-6-chloromethylpyrimidine-5-carboxylic acid, 2,3-difluoro or 2,3-dichloro-
quinoxaline-6-carboxylic acid or -6-sulphonic acid, 2-chlorobenzothiazole or
-oxazole-5- or -6-carboxylic acid or -5- or -6-sulphonic acid, 1,4-difluoro, 1,4-dichloro
40 or 1,4-dibromophthalazine-6-carboxylic acid or -6-sulphonic acid, 2,4-dichloroquin-
azoline-6- or -7-carboxylic acid, 2,3-dichloro-quinoxaline-7-carboxylic acid or -7-
sulphonic acid, 4,5-dichloro-6-pyridazon-1-yl-trimethylene carboxylic acid or -1',4'-
phenylene carboxylic acid.

45 Mentioned as further reactive groups are: trichloropyridazinyl, dichloro-1,2,4-
triazinyl, 3-chloropyridazine-6-carboxylic acid, 5-chloro-1,2,4-thiadiazol-3-yl-1',4'-
phenylene carboxylic acid, allylsulphone and allylsulphide radicals. Mention can also
be made of the reactive radical Z having, e.g. instead of a reactive halogen atom or
an ester group, a reactive ammonium, quinuclidinium, pyridinium, hydrazinium or
sulphonium radical or the sulphonic acid group.

50 In the preferred fibre-reactive anthraquinone dyestuffs of the Formula I,

Z represents the radical of a 6-membered, optionally benzo-condensed aromatic
nitrogen containing heterocycle, having a reactive halogen, advantageously the radical
of the cyanuric chloride, or 2,4,6-trifluoro-5-chloropyrimidine or the acyl radical of a
carboxylic acid halide having a polyhalogen containing azine radical, especially of
55 the 2,4-dichloropyrimidine-5- or -6-carboxylic acid chloride; or the acyl radical of
an N-alkyl-N-(2-halogen-4-alkoxy-s-triazinyl-6-)-carbamic acid halide; such as the
radical of N-ethyl-N-(2-chloro-4-methoxy-s-triazinyl-6)-carbamic acid chloride or the
acyl radical of an unsaturated or saturated aliphatic halogen carboxylic acid halide,
advantageously of β -bromoacrylic acid chloride, β -chlorocrotonic acid chloride or α,β -
60 dibromopropionic acid chloride.

The new fibre-reactive anthraquinone dyestuffs of the general Formula I are obtained, e.g. by condensing an aminoanthraquinone dyestuff of the general Formula II,



(II)

wherein X and Y have the meaning given in Formula I, with an acylating agent that contains a fibre-reactive radical Z, whereby the latter can form with the substrate at least one covalent bond, to obtain a fibre-reactive anthraquinone dyestuff of the general Formula I.

The starting materials of the Formula II and the production thereof are described in British Patent Application No. 48487/69. (Serial No. 1,277,439).

The following compounds of the Formula II have thereby proved to be especially suitable for the present process:

- 1 - amino - 4 - [3',4' - dimethyl - 5' - (3'' - aminophenyl - 1'') - disulfimido]-phenylamino - anthraquinone - 2 - sulphonic acid;
 - 1 - amino - 4 - [3',4' - dimethyl - 5' - (3'' - aminophenyl - 1'') - disulfimido]-phenylamino - anthraquinone - 2,6- and 2,7 - disulphonic acid;
 - 1 - amino - 4 - [3',4' - dimethyl - 5' - (3'' - aminophenyl - 1'') - disulfimido]-phenylamino - anthraquinone - 2,4'' - disulphonic acid;
 - 1 - amino - 4 - [3',4' - dimethyl - 5' - (3'' - aminophenyl - 1'') - disulfimido]-phenylamino - anthraquinone - 2,6,4'' - trisulphonic acid;
- as well as a mixture of
- 1 - amino - 4 - [3',4' - dimethyl - 5' - (3'' - aminophenyl - 1'') - disulfimido]-phenylamino - anthraquinone - 2,5 and 2,8 or 2,6 and 2,7 - disulphonic acid; or
 - 1 - amino - 4 - [3',4' - dimethyl - 5' - (3'' - aminophenyl - 1'') - disulfimido]-phenylamino - anthraquinone - 2,5,4'' and 2,8,4'' - trisulphonic acid.

Suitable compounds introducing the reactive radical Z are accordingly those initially mentioned under Z; if carboxylic and sulphonic acids are concerned, the chlorides or anhydrides of these are advantageously used.

The reaction of the aminoanthraquinone dyestuffs of the Formula II with a compound introducing the reactive radical Z is performed in the usual manner, advantageously in aqueous medium, optionally in the presence of inert, easily-removable, organic solvents such as lower aliphatic ketones, e.g. acetone, and preferably in the presence of mineral-acid-buffering agents such as sodium or potassium carbonate, sodium or potassium hydroxide, di- or trisodium or di- or tripotassium phosphate, or sodium or potassium acetate.

After completion of the reaction, the finished fibre-reactive anthraquinone dyestuff of the Formula I is salted out with sodium chloride or potassium chloride from its, advantageously previously neutralised, solution or suspension, filtered with suction, washed and dried. The new fibre-reactive anthraquinone dyestuffs are advantageously dried with a moderate heat and, optionally, under reduced pressure.

The new fibre-reactive anthraquinone dyestuffs are dark powders which, in the form of their alkali salts, are easily soluble in water. They are suitable for the dyeing and printing of textile material, especially that made from natural or regenerated cellulose fibres such as rayon staple, jute, linen, ramie, hemp and, in particular, cotton, in pure brilliant blue shades.

These materials are dyed with the reactive dyestuffs, obtainable according to the invention, using known methods. The cellulose material is impregnated or printed at a lower temperature, e.g. at 20—50° C., with the optionally thickened dyestuff solution and the dyestuff is then fixed by treatment with acid-binding agents. Suitable as such are, e.g. sodium carbonate, potassium carbonate, di- and tri-sodium phosphate, sodium hydroxide solution and, at temperatures above 50° C., also potassium or sodium bicarbonate. Instead of subjecting the impregnated materials to an alkaline aftertreatment, the acid-binding agent can in many cases be added, preferably in

the form of alkali carbonates, to the impregnating liquors or printing pastes and the production of the dyeing then effected by a short heating or steaming to temperatures between 100° C. and 160° C., or by a longish standing time at room temperature. The addition of hydrotropic agents to the printing pastes and impregnating liquors is advantageous in this process, e.g. the addition of urea in amounts of 10 to 200 g per litre of dyeing agent.

Furthermore, cellulose material can be dyed, with dyestuffs according to the invention, also using the exhaustion process by introducing the cellulose to be dyed into the dye bath containing an acid-binding agent and, optionally, also neutral salts such as, e.g. sodium chloride or sodium sulphate, dyeing being performed in a long dye liquor and at slightly elevated temperature. The dye bath is gradually heated to temperatures of 40 to 100° C. and the dyeing process completed at this temperature. The neutral salts, accelerating the extraction of the dyestuff, can be added to the dye bath optionally also after the actual dyeing temperature has been attained.

By the treatment with acid-binding agents, the new dyestuffs are chemically fixed to the fibre. After soaping for the purpose of removing non-fixed dyestuff, the cellulose dyeings have excellent fastness to wet-processing such as, in particular, to washing, water, perspiration, alkali and rubbing, as well as a good fastness to light.

Non-fixed dyestuff can be very easily and completely washed out. This property is an essential prerequisite for good wet-fastness of the dyeings on cellulose fibres using reactive dyestuffs.

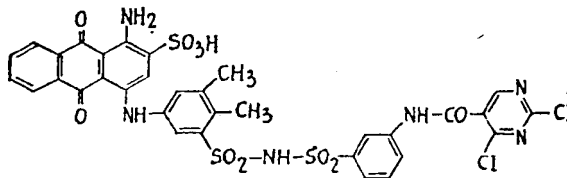
Moreover, with regard to the aftertreatment using agents for improving the fastness to wet-processing and/or creasing, the shade and fastness to light of the cellulose dyeings, obtained with the new dyestuffs, are only negligibly affected.

The new fibre-reactive anthraquinone dyestuffs can, however, also be used for the dyeing of polyamide-containing fibre material, e.g. natural fibre material such as wool or silk, or synthetic material such as nylon. Natural polyamide fibres are dyed in a hot, slightly acid bath, e.g. an acetic acid bath, in the presence of auxiliary agents to improve the evenness of the dyeing, such a fatty acid alkanolamine polycondensation products as well as, optionally, in the presence of salts such as sodium chloride or sulphate. Synthetic polyamide fibres are advantageously dyed in a hot acid bath, then rinsed and subsequently treated in a boiling alkaline bath.

Further details are given in the following Examples, whereby the temperatures are given in degrees Centigrade. In each case in the dyestuff formulae, the free acid form —SO₃H is given; the dyestuffs are, however, advantageously obtained in the form of their alkali metal salts or ammonium salts.

EXAMPLE 1

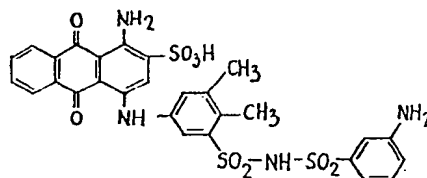
65.6 g of 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2-sulphonic acid are dissolved in 1200 ml of water with a pH-value of 6—7 and at room temperature. After cooling to 0—5°, 22.5 g of 2,4-dichloropyrimidine-5-carboxylic acid chloride are added to this solution. The pH-value of the reaction mixture is maintained at 5—6 by addition of a 10% solution of tertiary sodium-o-phosphate. As soon as the condensation reaction has finished, the dyestuff solution is heated to 20°, the pH-value adjusted to 7.0 and, by addition of 130 g of potassium chloride, the new anthraquinone reactive dyestuff is precipitated of the formula:



The dyestuff is filtered with suction, washed with 10% potassium chloride solution and dried at 60° in vacuo.

The 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2-sulphonic acid is obtained by dissolving 46.1 g of 3,3'-diamino-5,6-dimethyldibenzendisulphimide in 450 ml of water at 50° with a pH-value of 7—8 and adding to this solution, 38.2 g of 1-amino-4-bromoanthraquinone-2-sulphonic acid and 4 g of sodium bicarbonate. The reaction mixture is heated to 85—87° and to the solution is added in portions and

within one hour, a mixture of 0.5 g of copper powder and 20 g of sodium bicarbonate. The reaction is completed during 4 hours at 80—85°, the dyestuff solution separated from undissolved materials by filtration and the dyestuff of the formula

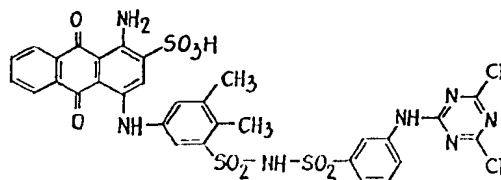


5 is precipitated with 32 g of sodium chloride. It is filtered and subsequently washed with 5% sodium chloride solution. 5

If cotton is padded with a solution, consisting of 20 g of the reactive dyestuff according to Example 1, and 20 g of sodium bicarbonate in 1000 ml of water, dried and thereupon exposed for 2 minutes to a dry heat of 140°, then a very pure, blue dyeing is obtained which, after soaping, exhibits a very good fastness to wet processing and to light. 10 10

EXAMPLE 2

65.6 g of 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2-sulphonic acid are dissolved in 1200 ml of water with a pH-value of 6—7 and at room temperature. After cooling to 0—5°, 19.5 g of cyanuric chloride are added to this solution. The pH-value of the reaction mixture is maintained at 5—6 by addition of a 10% solution of tertiary sodium-o-phosphate. As soon as the condensation reaction has finished, the dyestuff solution is heated to 40°, the pH-value adjusted to 7.0 and, by addition of 130 g of potassium chloride, the new anthraquinone reactive dyestuff is precipitated of the formula: 15 20

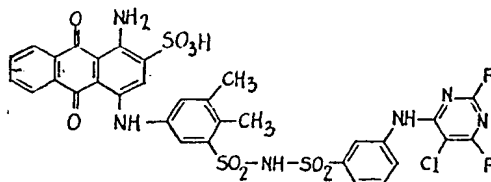


The dyestuff is filtered with suction, washed with 10% potassium chloride solution and dried at 60° in vacuo.

25 If cotton is padded with a solution, consisting of 20 g of the reactive dyestuff according to Example 2, and 20 g of sodium bicarbonate in 1000 ml of water, dried and thereupon exposed for 5 minutes to a dry heat of 140°, then a very pure, blue dyeing is obtained which, after soaping, exhibits a very good fastness to wet processing and to light. 25

EXAMPLE 3

30 65.6 g of the dyestuff 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2-sulphonic acid, according to Example 1, are dissolved in 1200 ml of water with a pH-value of 6—7. To this solution are added dropwise, at a temperature of 5—10°, 20.7 g of 2,4,6-trifluoro-5-chloropyrimidine and the pH-value is maintained at 6—7 by the dropwise addition of 10% sodium carbonate solution. The obtained reactive dyestuff of the formula 35



precipitates from the reaction mixture and, after completion of the reaction, is filtered

off, washed with 3% sodium chloride solution and dried at 50° in vacuo.

If wool fabric is treated with a 2% aqueous solution of the dyestuff of the above formula, which also contains 2.4% of acetic acid, during 15 minutes at 80°, then a strong blue dyeing is obtained having a good fastness to light and a very good fastness to wet processing.

5 If instead of the 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-di-
sulphimido]-phenylamino-anthraquinone-2-sulphonic acid according to Example 3
equivalent amounts of the aminoanthraquinone dyestuffs listed in Table I, Column II,
or of the stated mixtures are used, and in place of the 2,4,6-trifluoro-5-chloro-
10 pyrimidine, equivalent amounts of the acylating agent given in Column III, with
otherwise the same procedure as described in Example 3 at temperatures given in
Column IV, then reactive blue anthraquinone dyestuffs are obtained having similarly
valuable properties.

5

10

TABLE I

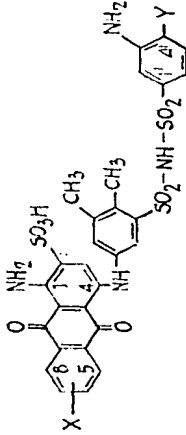
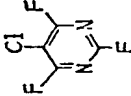
I	II	III	IV
Example No.		Acylating agent	Temperature in °C.
4	X	Cl-CO-CHBr-CH ₃ -Br	5-10
5	H	ClCO-CH=CHBr	5-10
6	H	ClCO-CH ₂ Cl	5-10
7	7-SO ₃ H	Cl-CO-CH=CCl-CH ₃	5-10
8	H	ClCO-CH=C(CH ₃)Cl	5-10
9	6-SO ₃ H		5-10

TABLE I

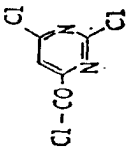
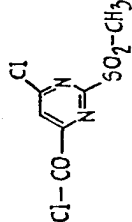
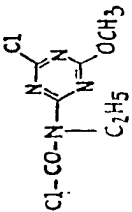
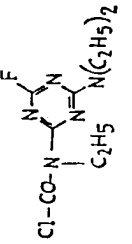
I	II		III	IV
	X	Y		
10	H	H	 <chem>ClC1=NC(Cl)=NC(Cl)=C1</chem>	5-10
11	5/8-SO ₃ H(mixture)	SO ₃ H	 <chem>ClC1=NC(Cl)=NC(S(=O)(=O)O)=C1</chem>	5-10
12	5/8-SO ₃ H(mixture)	H	Cl-CO-C≡CCl	5-10
13	H	H	Cl-CO-CH=CH ₂	5-10
14	6-SO ₃ H	H	Br-CO-CHBr-CH ₂ -Br	5-10
15	H	H	 <chem>ClC1=NC(Cl)=NC(OC)=C1</chem>	5-10
16	7-SO ₃ H	H	 <chem>ClC1=NC(Cl)=NC(S(=O)(=O)O)=C1</chem>	0-5

TABLE I (Continued)

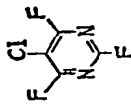
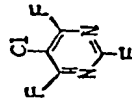
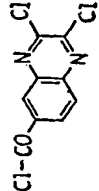
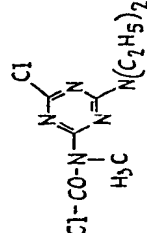
I	II	III	IV
Nr	X	Y	
17	7-SO ₃ H	H	 <chem>Fc1nc(F)c(Cl)n1</chem> 15-20
18	6/7-SO ₃ H(mixture)	H	 <chem>Fc1nc(F)c(Cl)n1</chem> 15-20
19	H	H	 <chem>ClC1=NC(Cl)=NC(Cl)=N1</chem> 5-10
20	H	H	 <chem>CCN(CC)C1=NC(Cl)=NC(Cl)=N1</chem> 0-5

TABLE I (Continued)

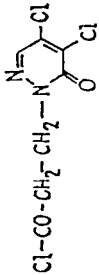
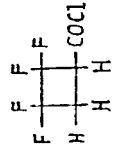
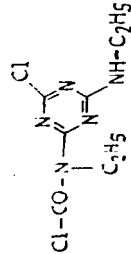
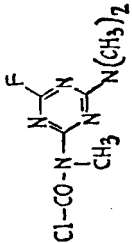
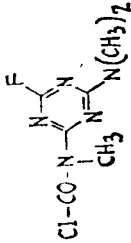
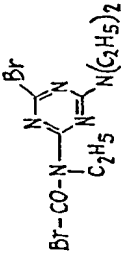
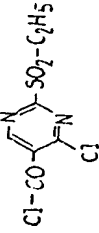
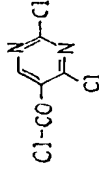
I	II	III	IV
Nr	X	Y	
21	5/8-SO ₃ H(mixture)	H	
22	7-SO ₃ H	H	
23	6-SO ₃ H	H	
24	H	H	
25	6-SO ₃ H	H	

TABLE I (Continued)

I	II	III	IV
Nr	X	Y	
26	7-SO ₃ H	H	
27	7-SO ₃ H	H	
28	6-SO ₃ H	H	

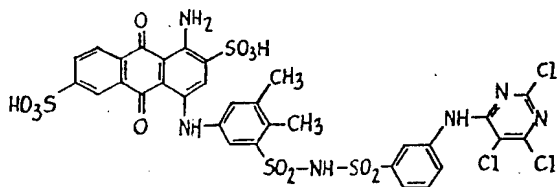
EXAMPLE 29

73.6 g of 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2,6-disulphonic acid (produced from 1-amino-4-bromo-anthraquinone-2,6-disulphonic acid and 3,3'-diamino-5,6-dimethylbenzene-disulphimide analogously to the data in Example 1) are dissolved in 1300 ml of water and to the solution are added 22.9 g of tetrachloropyrimidine at 80—85°. The reaction mixture is stirred at 80—85° until the reaction is completed. The pH-value is maintained at 6—7 by the addition of 20% sodium carbonate solution. As soon as the reaction is completed, the dyestuff solution is filtered and the dyestuff then precipi-

5

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rated by the addition of 230 g of solid sodium chloride. The dyestuff is filtered off, subsequently washed with 20% sodium chloride solution and dried in vacuo at 80°. It corresponds to the formula:



5 If, instead of 1-amino-4-[3'4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2,6-disulphonic acid, equivalent amounts are used of the aminoanthraquinone dyestuffs, given in Table II, Column II, or of the stated mixtures
10 and, instead of tetrachloropyrimidine, the acylating agents given in Column III, the procedure being otherwise as described in the Example and at temperatures given in Column IV then similarly valuable blue reactive anthraquinone dyestuffs are obtained.

5

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TABLE II

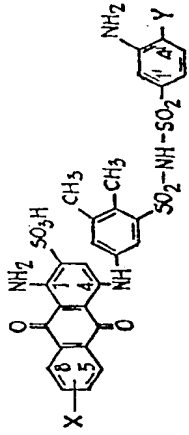
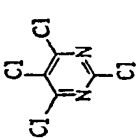
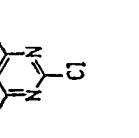
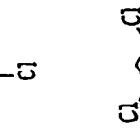
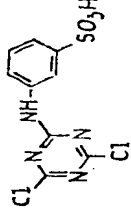
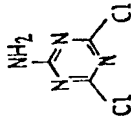
I	II	III	IV
Example No.		Acyating agent	Temperature in °C.
	X	Y	
30	5/8-SO ₃ H(mixture)		80—90
31	7-SO ₃ H		80—90
32	5/8-SO ₃ H(mixture)		80—90

TABLE II (Continued)

I	II	III	IV
Nr	X	Y	
33	H	H	
34	6-SO ₃ H	H	

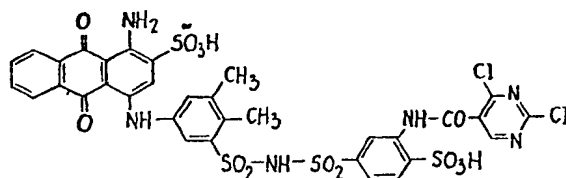
EXAMPLE 35

32.8 g of 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2,4''-disulphonic acid are dissolved in 450 ml of water at 30° and having a pH-value of 8.5—9.0. The pH-value is adjusted to 3.0 by the addition of 10% hydrochloric acid and the solution is cooled to +3°, whereby a solution of 11.6 g of 2,4-dichloropyrimidine-5-carboxylic acid chloride dissolved in 40 ml of acetone is added dropwise within 5 minutes. The pH-value is maintained at 2.0—3.0 by the addition of 10% sodium hydroxide solution. The temperature being between 0 and 5°. As soon as the reaction is completed, the pH-value of the reaction

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mixture is adjusted to 7.0 and the partially already precipitated reactive dyestuff of the formula



- 5 is salted out by the addition of 70 g of solid sodium chloride, filtered off and sub-
sequently washed with 15% sodium chloride solution. Drying is performed at 50—
60° in vacuo. The dyestuff dissolves in water to give a blue colour and dyes cotton,
according to the process given in Example 1, in very pure blue shades. The thus
obtained dyeing exhibits after soaping an excellent fastness to wet-processing and to
light.
- 10 If instead of the 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-di-
sulphimido]-phenylamino-anthraquinone-2,4''-disulphonic acid, equivalent amounts of
the aminoanthraquinone dyestuffs are used which are listed in Table III, Column II,
or of the stated mixtures and, instead of 2,4-dichloropyrimidine-5-carboxylic acid
chloride, equivalent amounts are used of the acylating agents given in Column III,
15 the procedure being otherwise as described in the Example and at temperatures given
in Column IV then blue, reactive anthraquinone dyestuffs are obtained having
similarly valuable properties.

TABLE III

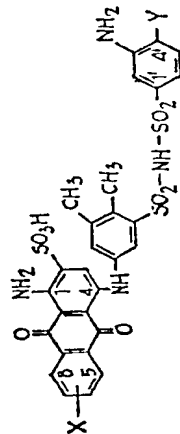
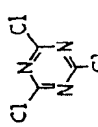
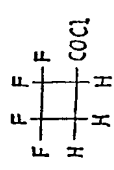
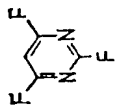
I	II	III	IV
Example No.		Acyating agent	Temperature in °C.
36	<div>X</div> <div>H</div>	<div>Y</div> <div>SO₃H</div>	<div> $\text{H}_2\text{C}-\underset{\text{Br}}{\underset{\text{Br}}{\text{CH}}}-\text{COCl}$ </div> <div>5-10</div>
37	5/8-SO ₃ H(mixture)	H	<div>  </div> <div>5-10</div>
38	6-SO ₃ H	H	<div>  </div> <div>5-10</div>
39	H	H	<div>  </div> <div>15-20</div>

TABLE III (Continued)

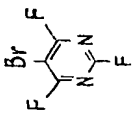
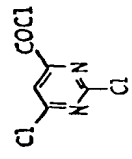
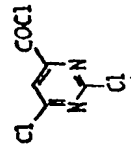
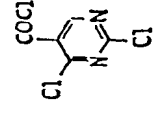
I	II		III	IV
	X	Y		
40	H	H		10-15
41	H	SO ₃ H	BrHC=CH-COCl	5-10
42	5/8-SO ₃ H(mixture)	H		5-10
43	6-SO ₃ H	H		5-10
44	6-SO ₃ H	SO ₃ H		5-10

TABLE III (Continued)

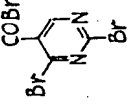
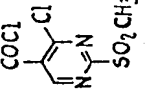
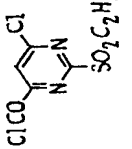
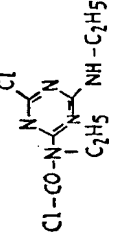
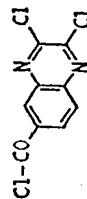
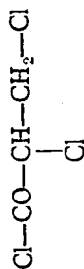
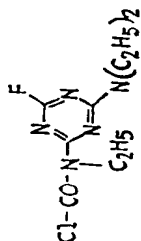
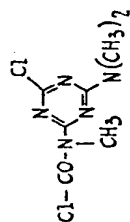
I	II		III		IV
Nr	X	Y			
45	H	H			5-10
46	6-SO ₃ H	H			0-5
47	7-SO ₃ H	H			0-5
48	H	H			10-15

TABLE III (Continued)

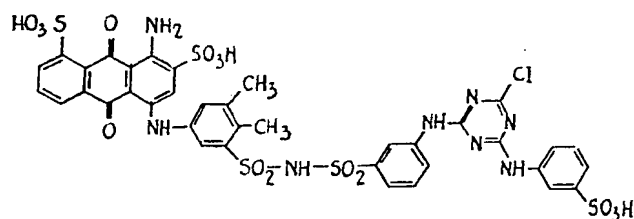
I	II		III	IV
	Nr.	X	Y	
49	6-SO ₃ H		H	10-20
50	H		H	0-5
51	H		H	0-5
52	7-SO ₃ H		H	5-10



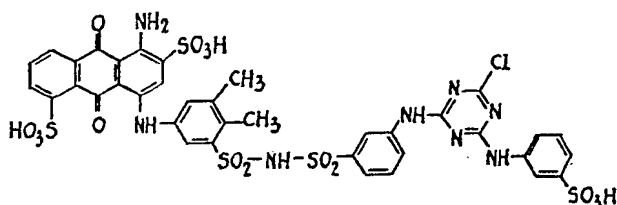
EXAMPLE 53

36.8 g of a mixture of 1-amino-4-[3',4'-dimethyl-5'-(3''-aminophenyl-1'')-disulphimido]-phenylamino-anthraquinone-2,8- and -2,5-disulphonic acid are dissolved in 500 ml of water (neutral) at a temperature of 40-45°. Into this solution are sprinkled, while stirring, 17.6 g of 1-[N-2',4'-dichloro-s-triazinyl-6']-aminobenzene-3-sulphonic acid. During the reaction, the pH - value is maintained at 6-7 by the dropwise addi-

tion of 20% soda solution. The reaction is completed at 40—45° and the dyestuff mixture of the formulae



and



precipitated by the addition of solid potassium chloride, filtered off and subsequently washed with 20% potassium chloride solution. The dyestuff mixture is dried in vacuo at 70°. It dyes cotton, using the method described in Example 1, in pure blue shades. The dyeings are distinguished by a very good fastness to wet processing.

If, instead of the anthraquinone dyestuff mixture stated in this Example, equivalent amounts are used of the anthraquinone dyestuffs listed in Column II of Table IV or of the therein stated mixtures and, instead of the 1-(N-2',4'-dichloro-5-triazinyl-6')-aminobenzene-3-sulphonic acid, the acylating agents given in Column III are used, the procedure being otherwise as described in the Example and at temperatures given in Column IV then similarly valuable blue reactive anthraquinone dyestuffs are obtained.

TABLE IV

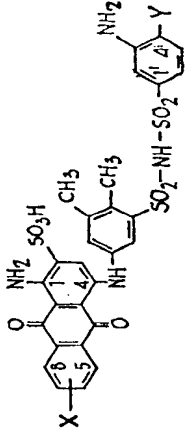
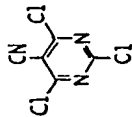
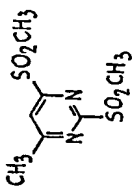
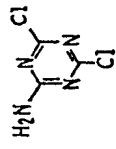
I Example No.	II	III Acylation agent	IV Temperature in °C
			
54	6-SO ₃ H		25—35
55	H		40—50
56	7-SO ₃ H		30—40

TABLE IV (Continued)

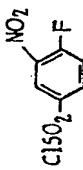
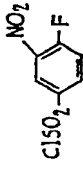
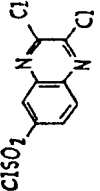
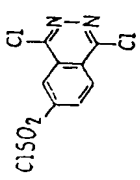
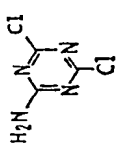
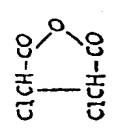
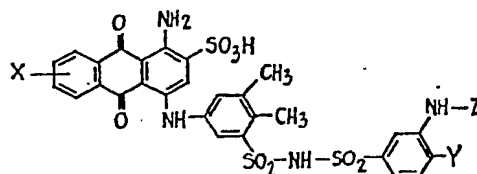
I	II		III	IV
	X	Y		
57	6-SO ₃ H	H	CH ₂ =CH-SO ₂ Cl	20-30
58	H	H	ClCH=CH ₂ -SO ₂ Cl	20-30
59	6-SO ₃ H	H	 <chem>ClS(=O)(=O)c1ccc([N+](=O)[O-])cc1F</chem>	20-30
60	7-SO ₃ H	H	 <chem>ClS(=O)(=O)c1ccc([N+](=O)[O-])cc1F</chem>	20-30
61	5/8-SO ₃ H(mixture)	H	 <chem>ClS(=O)(=O)c1ccc2nc(Cl)c(Cl)nc2c1</chem>	20-30

TABLE IV (Continued)

I	II		III	IV
	X	Y		
Nr.				
62	6-SO ₃ H	H		20-30
63	H	H		30-40
64	H	H	CH ₂ =CH-SO ₂ Cl	20-30
65	7-SO ₃ H	H	CH ₂ =CH-SO ₂ Cl	20-30
66	H	H		20-30

WHAT WE CLAIM IS:—

1. Fibre-reactive anthraquinone dyestuffs of the general Formula I



(I)

wherein

5 X and Y represent independently of each other hydrogen or the sulphonic acid group, and

Z represents a fibre-reactive radical capable of forming with the substrate at least one covalent bond.

10 2. Fibre-reactive anthraquinone dyestuffs as claimed in Claim 1 wherein the radical Z is the radical of a 6-membered, optionally benzocondensed, aromatic nitrogen containing heterocycle having a reactive halogen, or the acyl radical of a carboxylic acid halide having a polyhalogen-containing azine compound or the acyl radical of an N-alkyl-N-(2-halogeno-4-alkoxy-s-triazinyl-6)-carbamic acid halide.

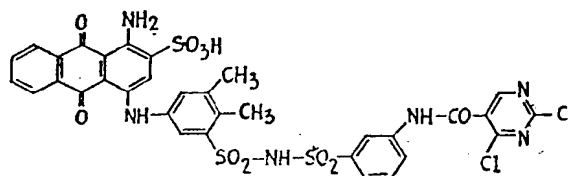
15 3. Fibre-reactive anthraquinone dyestuffs as claimed in Claim 1 wherein the radical Z is the acyl radical of an unsaturated or saturated aliphatic halogen carboxylic acid halide.

4. Fibre-reactive anthraquinone dyestuffs as claimed in Claim 2 wherein the radical Z is the cyanuric chloride radical or the acyl radical of N-ethyl-N-(2-chloro-4-methoxy-s-triazinyl-6)-carbamic acid chloride.

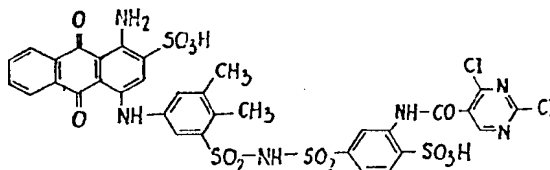
20 5. Fibre-reactive anthraquinone dyestuffs as claimed in Claim 2 wherein the radical Z is the radical of 2,4,6-trifluoro-5-chloropyrimidine or the acyl radical of 2,4-dichloropyrimidine-5- or -6-carboxylic acid chloride.

25 6. Fibre-reactive anthraquinone dyestuffs as claimed in Claim 3 wherein the radical Z is the acyl radical of β -bromoacrylic acid chloride, β -chlorocrotonic acid chloride or α,β -dibromopropionic acid chloride.

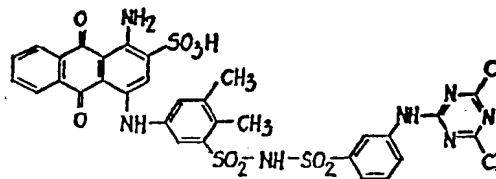
7. A fibre-reactive anthraquinone dyestuff as claimed in Claim 1 which is of the formula



30 8. A fibre-reactive anthraquinone dyestuff as claimed in Claim 1 which is of the formula



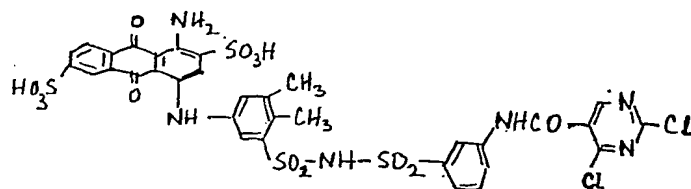
9. A fibre-reactive anthraquinone dyestuff as claimed in Claim 1 which is of the formula



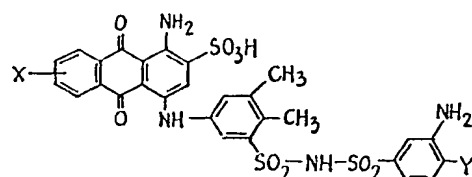
35

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10. A fibre-reactive anthraquinone dyestuff as claimed in Claim 1 which is of the formula



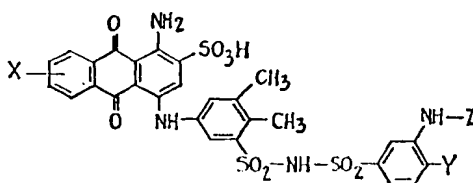
11. Process for the production of reactive anthraquinone dyestuffs as claimed in Claim 1 characterised by condensing an amino-anthraquinone dyestuff of Formula II



(II)

wherein

X and Y represent independently of each other hydrogen or the sulphonic acid group with an acylating agent that contains a fibre-reactive radical Z, to obtain a fibre-reactive anthraquinone dyestuff of Formula I



(I)

wherein X, Y and Z have the meanings given above.

12. Process for the dyeing or printing of textile fibre material characterised by the use of reactive anthraquinone dyestuffs as claimed in any of Claims 1 to 10.

13. Process according to Claim 12 characterised in that the fibre material is polyamide or natural or regenerated cellulose.

14. Textile fibre material dyed or printed by the use of the reactive anthraquinone dyestuff as claimed in any of Claims 1 to 10.

15. Manufacture of fibre-reactive anthraquinone dyestuffs according to Claim 1 substantially as described with reference to any of the foregoing Examples.

16. Fibre-reactive anthraquinone dyestuffs as claimed in Claim 1 whenever prepared or produced by a process of manufacture hereinbefore described.

17. A fibre-reactive anthraquinone dyestuff as claimed in Claim 1 and identified by any of the foregoing Examples 1, 3, 14, 19, 25, 28, 30, 35, 37, 53, 64 and 66.

18. A fibre-reactive anthraquinone dyestuff as claimed in Claim 1 and identified by any of the foregoing Examples 2, 4—13, 15—18, 20—24, 26, 27, 29, 31—34, 36, 38—52, 54—63 and 65.

V. GALLAFENT & CO.,
Chartered Patent Agents,
8, Staple Inn, London, W.C.1.

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